



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US92/06928 (22) International Filing Date: 20 August 1992 (20.08.92) (30) Priority data: 747,832 21 August 1991 (21.08.91) US (71) Applicant: EASTMAN KODAK COMPANY [US/US]; 343 State Street, Rochester, NY 14650-2201 (US). (72) Inventor: SKOCHDOPOLE, Todd, Richard ; 248 Carling Road, Rochester, NY 14610 (US). (74) Agent: GERLACH, Robert, A.; 343 State Street, Roches- ter, NY 14650-2201 (US).		(81) Designated States: JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE). Published <i>With international search report.</i>
(54) Title: PHOTOGRAPHIC POLYOLEFIN COATED PRINT MATERIALS (57) Abstract Photographic polyolefin coated print materials having improved stability, the polyolefin layer containing titanium dioxide pigment, a hindered amine light stabilizing agent and zinc oxide.		

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Photographic Polyolefin Coated Print Materials
Background of the Invention
Field of the Invention

This invention relates to resin coated
5 photographic print materials and more particularly to
photographic papers and paper-like materials.

Polyolefin coated papers suffer from a
disadvantage in that when exposed to light,
photodegradation occurs resulting in embrittlement of
10 the polyolefin layer due to a loss in molecular weight.
When a photographic print is exposed to variations in
temperature and/or humidity, it is believed that
differential forces are created due to the mismatch of
the respective thermal and humidity expansion
15 properties of adjacent layers. Since these forces are
relatively small, the polyethylene layer in a
relatively new print can resist them. However, as
aging occurs, the polyethylene layer becomes more
brittle and as a result of these forces, microcracks
20 commonly called crazes form in the resin layer. Once
crazing occurs, the image quality deteriorates and
eventually, once the crazing is severe enough, the
print is destroyed.

This degradation of polyolefin layers is
25 accelerated by the presence of TiO_2 which is necessary
to provide the opacity and reflectance required for
photographic prints. TiO_2 is unique amongst white
pigments for this purpose because its refractive index
permits its use in smaller quantities than others.
30 Higher concentration of pigments result in dispersion
problems as well as economic disadvantages.

Description of Related Art

U.S. Patents 4,562,145 and 4,582,785 disclose
certain hindered amine light stabilizers (HALS) in the
35 polyolefin layer of a resin coated photographic paper
to prolong the life of a photographic print in an
uncracked form. The polyolefin layer may also contain

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conventional additives including pigments, dyestuff, optical brighteners and the like.

Summary of the Invention

This invention provides a resin coated
5 photographic print material including a paper-like substrate coated with a layer of a polyolefin resin wherein the polyolefin resin layer contains from about 5 to 25 percent by weight of titanium dioxide pigment, at least 0.01 percent by weight of a hindered amine
10 light stabilizer and from about 0.5 to about 4 percent by weight of zinc oxide. It was surprisingly found that the combination of small quantities of hindered amine light stabilizer compounds and zinc oxide added to polyolefin resins coated onto a paper like support
15 improved the stability of the polyolefin coated support by a factor of at least 3 and usually by a factor of 5 or 6 times comparable polyolefin coated substrate containing only a hindered amine light stabilizer as the sole stabilizing agent.

20 Detailed Description of the Invention

Throughout this application the following terms have the meanings assigned hereto:

Paper-like - this terms includes paper materials which have widespread use in the photographic
25 industry as print materials in addition to substrates such as microvoided matrix materials described in U.S. Patents 4,994,312 and 4,770,931, each of which is incorporated wholly herein by reference. A particularly applicable material of this type is one
30 having a matrix material of polyethylene terephthalate containing crosslinked microbeads, the material which when oriented in both the machine and transverse direction results in a microvoided sheet material having a white appearance similar to paper.

35 Hindered amine light stabilizers compounds containing a 2,2,6,6-tetramethyl-piperidine moiety and include, for example, bis(2,2,6,6-tetramethyl-4-piperidiny1)sebacate, bis(1,2,2,6,6,-pentamethyl-4-

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piperidiny)sebacate, n-butyl-(3,5-di-tert-butyl-4-hydroxybenzyl)bis-(1,2,2,6,6-pentamethyl-4-piperidiny)malonate, dimethyl succinate polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidiny)-1,6-N'-bis(2,2,6,6-tetramethyl-4-piperidiny)-1,3,5-hexanediamine polymer with 2,4,6-trichloro-1,3,5-triazine and 2,4,4-trimethyl-1,2-pentanamine, poly(6-morpholino-s-triazine-2,4-diyl)[(2,2,6,6-tetra-methyl-4-piperidyl)imino]]. These materials are available under the tradenames Tinuvin 770, Tinuvin 765, Tinuvin 144, Tinuvin 622LD, Chimassorb 944FL and HALS 1, respectively, available from Ciba-Geigy. The HALS should be present in the polyolefin layer in an amount of at least about 0.01 percent by weight, preferably from 0.01 to about 2 percent by weight, preferably from 0.01 to about 0.05 percent by weight. The upper limit is set solely from an economic view as a point is reached where additional amount of the HALS does not increase the stability.

The resin coated photographic print material in accordance with this invention is prepared by blending the various ingredients, including the polyolefin polymer, titanium dioxide in an amount of from about 5 to about 25 percent by weight and most preferably from about 8 to about 15 percent by weight based on the total weight of the formulation for the olefin layer, the hindered amine light stabilizing agent and from about 0.5 to 4 percent by weight, zinc oxide, preferably from about 0.5 to about 3.5 percent by weight plus other optional addenda and melt extruding the polyolefin containing composition onto the surface of a photographic paper or paper like substrate in accordance with procedures well known in the photographic paper forming industry. The substrate may be coated on one or both sides but preferably is coated on both sides thereof. Generally, the substrate

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is coated on the emulsion side with a pigmented polyolefin and on the other side with a clear or unfilled polyolefin. The polyolefin layer on the emulsion side serves two functions, to prevent wetting of the paper during film processing and to provide the necessary opacity and reflectance properties.

In a preferred method of making the resin coated paper in accordance with this invention, the masterbatch technique is employed wherein high concentrations of appropriate ingredients, such as TiO_2 , ZnO , hindered amine light stabilizer and the like are compounded into the polyolefin in a suitable apparatus, such as, a twin screw extruder. The master batch is then blended with virgin polyolefin to which various addenda are added to achieve the desired final composition. This composition is then extrusion coated by known methods unto the paper like substrate in the coverage desired.

Any suitable polyolefin resin generally used in the preparation of photographic print material may be employed in accordance with this invention such as for example, polyethylene, polypropylene, including mixtures thereof as well as such polymers having different densities such as, low density polyethylene, high density polyethylene, and the like. Pigments other than titanium dioxide may be employed in minor amounts in order to provide the desired opacity to the polyolefin layer as well as to provide the necessary reflectance properties to display the image resulting from the light sensitive layers that are built onto the photographic print material in accordance with this invention, however, TiO_2 as the sole white pigment is preferred. Other white pigments include material barium sulphate, antimony trioxide, and the like. Additional addenda may be incorporated into the polyolefin layer including optical brightening agents, colored pigments, dyestuffs, antistatic agents and the like.

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The various layers to convert the paper support into a light reflecting photographic print material, such as silver halide emulsion layers, subbing layers, interlayers and overcoat layers are provided on to the polyolefin coated paper support. The silver halide emulsions employed in the present invention preferably comprise silver chloride grains which are at least 80 mole percent silver chloride and the remainder silver bromide. The silver chloride is preferably present in an amount of at least 90 mole percent and most preferably in an amount of at least 95 mole percent because of the improved speed in processing of the print material.

The silver halide emulsions comprise vehicles conventional in the art. Preferred vehicles are hydrophilic colloids which can be employed alone or in combination with hydrophobic materials. Preferred hydrophilic colloids are gelatin, for example, alkali-treated gelatin or acid-treated gelatin, and gelatin derivatives such as acetylated gelatin and phthalated gelatin.

The silver halide emulsions can be chemically and spectrally sensitized as in common in the art. The emulsions, or other layers of the material, can contain stabilizers, antifoggants, and other components intended to prolong the useful life of the material prior to exposure or of the photographic image obtained after development.

The material will commonly contain one or more dye-forming couplers which will provide the final viewable image. However, other means of forming a viewable image can be employed.

The material will typically contain additional layers, such as subbing layers to improve adhesion to the support and interlayers and overcoat layers to separate and protect the sensitive layers and to carry stabilizers, filter dyes and the like.

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Further details of the components of the photographic reflection print material, the way they are prepared, and how they are processed to obtain a viewable image are provided in Research Disclosure, 5 Nov. 1979, Item No. 18716, published by Kenneth Mason Publications, Ltd., The Hold Harbouraster's, 8 North Street, Emsworth, Hampshire PO10 7DD, England and from Atwell U.S. Patent No. 4,269,927, issued May 26, 1981.

Print materials in accordance with this 10 invention as well as the control materials were subjected to accelerated aging conditions by incubation over a period of time with samples being taken periodically in order to measure the molecular weight of the polyolefin as a determination of the degree of 15 degradation resulting in the polymer. Both controls containing hindered amine light stabilizing agent as the sole stabilizing agent and with zinc oxide as the sole stabilizing agent were conducted in order to provide a standard from which the improvement can be 20 observed. Specific formulations together with the precise test conditions are set forth in the following examples in which parts and percentages are by weight unless otherwise indicated.

Example 1 (Comparison)

25 A medium density polyethylene resin was extrusion coated onto photographic paper at a thickness of 5.6 lbs/1000 ft². The opposite side of the paper was coated with polyethylene at a coverage of 6.0 lbs/1000 ft².

30 Example 2 (Comparison)

A masterbatch of 36 weight percent anatase TiO₂ was melt compounded with polyethylene using a twin extruder, extruded through an annular die, quenched into a waterbath and pelletized. This masterbatch 35 resin was then blended at a ratio of 1 part masterbatch resin to 2 parts pure polyethylene and then extrusion coated onto photographic paper at a coverage of 5.6

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lbs/1000 ft². The opposite side of the paper was coated similar to Example 1.

Examples 3 - 5

Masterbatches were prepared in a similar manner as described in Example 2, with the exception that various other additives as well as the TiO₂ were included; these formulations are shown in Table 1. The masterbatch resins in Examples 3 - 5 were blended and extrusion coated in a similar manner as Example 2, as well as extrusion coated on the opposite side of the paper as Example 1.

Table 1

Formulation (wt%)

Example No.	Anatase TiO ₂	ZnO	Chimassorb 944
3	12 (comparison)	3	0
4	12 (comparison)	0	0.10
5	12	3	0.10

A sample of the pigmented resin layer each of Examples 1 - 5 were measured for weight average molecular weight by gel permeation chromatography.

Samples of each of Examples 1 - 5 were exposed to a 100 footcandle light in an oven controlled to 80°C and 50% RH for 7, 14 and 28 days. Weight average molecular weight was remeasured of the pigmented resin layer on these aged samples. The loss of molecular weight of the polyethylene is an indication of its stability and thus related to crazing propensity. The results are shown in Table 2.

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Table 2.
Molecular Weight After Light Exposure
(Weight Average Mol Wt. X 1000)

Example No.	0 days	7 days	14 days	28 days
1	81.3	77.6	67.4	40.6
2	82.6	4.7	5.1	5.3
3	78.8	16.4	8.4	6.5
4	85.4	34.7	5.8	6.1
5	85.1	80.2	83.9	86.0

Table 2 shows that when pure polyethylene is exposed to light, it gradually decreases in molecular weight (Example 1). After TiO₂ is added (Example 2), light stability of the polyethylene is dramatically reduced. The addition of TiO₂ also increases L* and causes a shift in b* when measured for color properties using a Pacific Scientific Spectrogard, a spectrophotometer type colorimeter to measure 1976 CIE values for lightness (L*) and yellowness/blueness (b*). When ZnO and TiO₂ are added (Example 3), an improvement in light stability of polyethylene is observed compared to pure polyethylene, but there is essentially no change in the color properties of the sheet. An improvement in polyethylene light stability is also found when a HALS is used with TiO₂ (Example 4). However, when a HALS and ZnO are used in combination with TiO₂ (Example 5), in accordance with the invention, a very significant improvement in light stability is seen; in fact, essentially no degradation in molecular weight after 28 days at these severe conditions is observed.

Examples 6 - 10

A masterbatch of 1 weight percent Chimassorb 944 was compounded into polyethylene using a twin screw extruder as described in Example 2. Also compounded in the same manner was a second masterbatch containing 15 weight percent ZnO and a third masterbatch containing 45 weight percent anatase TiO₂. Examples 6 - 10 were

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made by using various blend ratios of these three masterbatches and pure polyethylene to extrusion coat onto photographic paper. The formulations for Examples 6 - 10 are shown in Table 3.

- 5 Two sets of samples from Examples 6 - 10 were exposed to the same accelerated aging conditions as Examples 1 - 5; however, these sets were cycled to room temperature twice weekly for examination, thus also exposing them to a temperature and humidity cycle. For 10 the first set of samples, the number of days required at the aging conditions to produce crazing of the pigmented polyethylene coated layer was measured. For the second set of samples, during their room temperature cycle they were wrapped around a 3/4 inch 15 mandrel, and then examined for crazing. The number of days required to produce crazing after the mandrel wrapping were thus measured. All of these results are listed in Table 3.

Table 3

Example No.	TiO ₂	Formulation (wt%)		Days to Craze	
		ZnO	Chimassorb 944	w/o Mandrel	w/Mandrel
6	12.2	0	0	31	11
7	12.2	3.0	0	91	28
8	12.2	0	.10	42	28
9	12.2	1.5	.05	210	139
10	12.2	3.0	.10	280	150

- 20 Table 3 again shows that both a HALS and ZnO can be used separately to improve the light stability (up to 3 times improvement in days to craze) of the resin coated layer. However, when a HALS and ZnO are used in combination, a much greater degree of light stability 25 (a 7 to 12 times improvement in days to craze) is found.

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Examples 6 - 10 were also measured for color properties regarding the 1976 CIE values for lightness (L^*) and yellowness/blueness (b^*) with the UV filter in the incident light. These values are recorded in Table 4.

5

Table 4

Example No.	CIELAB Values (UVO)	
	L^*	b^*
6	95.41	1.64
7	95.53	1.48
8	95.49	1.81
9	95.54	1.70
10	95.47	1.68

Comparison of Example 6, with only TiO_2 , and Examples 7 and 10 (both with 3% ZnO , Example 10 being the object of this invention) shows that the addition of the ZnO to the formulation has no impact on the color properties of the extrusion coated paper.

Examples 11 - 18

The masterbatches described in Examples 6 - 10 were used to produce extrusion coated paper containing various levels of Chimassorb 944, with all other components constant (3 weight percent ZnO and 12.2 weight percent anatase TiO_2).

Examples 11 - 18 were exposed to the same conditions as Examples 6 - 10, and measured for the number of days to craze, both with and without the mandrel wrapping. The results are shown in Table 5.

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Table 5

Examples No.	Wt% Chimassorb 944	Days to Craze	
		Without Mandrel	With Mandrel
11 (control)	0	63	28
12	.01	139	60
13	.03	160	91
14	.05	242	139
15	.07	270	139
16	.10	280	145
17	.15	280	156
18	.20	280	156

Table 5 shows that as little as 0.01 weight percent of a HALS, when used in combination with 3% ZnO, gives a significant improvement in light stability (a 2 time improvement over ZnO alone) of the polyethylene resin coated layer of photographic paper.

Example 19

To the pigmented layer of the support of Example 5 is coated, in order with the following layers, layer 1 being adjacent to the support to form a light sensitive element:

1. Blue sensitive layer:

Chemically and blue spectrally sensitized monodisperse silver chloride negative emulsion (0.34 g AG/m²) and yellow-dye forming coupler Y (1.08 g/m²) in di-n-butyl phthalate coupler solvent (0.27 g/m²), gelatin (1.51 g/m²)

2. Interlayer:

Gelatin (0.76 g/m²)

3. Green sensitive layer:

Chemically and green spectrally sensitized monodisperse silver chloride negative emulsion (0.27 g Ag/m²) and magenta-dye forming coupler M (0.42 g/m²) in di-n-butyl phthalate coupler solvent (0.22 g/m²), gelatin (1.24 g/m²)

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4. UV absorbing layer:

A mixture of hydroxyphenylbenzotriazoles (0.38 g/m²), gelatin (0.74 g/m²)

5. Red sensitive layer:

- 5 Chemically and red spectrally sensitized monodisperse silver chloride negative emulsion (0.18 g Ag/m²) and cyan-dye forming coupler C (0.42 g/m²) in di-n-butyl phthalate coupler solvent (0.24 g/m²), gelatin (1.08 g/m²)

10 6. UV absorbing layer:

A mixture of hydroxyphenylbenzotriazoles (0.38 g/m²), gelatin (0.74 g/m²)

7. Overcoat layer:

Gelatin (1.35 g/m²)

- 15 The layers 1 to 7 were hardened with bis(vinylsulfonyl)methyl ether at 1.8% of the total gelatin weight.

Coupler identifications are:

- C = Cyan dye forming coupler: 2-(α -2,4-di-tert-
20 amylophenoxy)butyramido)-4,6-dichloro-5-ethyl phenol
M = Magenta dye forming coupler: 1-(2,4,6-trichlorophenyl)-3-(2-chloro-5(α -(4-hydroxy-3-tert-butylphenoxy)-tetradecanoamido)anilino)-5-pyrazolone
Y = Yellow dye forming coupler: α -(4-(4-
25 benzyloxyphenyl-sulfonyl)phenoxy)- α -(pivalyl)-2-chloro-5-(Y-(2,4-di-t-

- amylophenoxy)butyramido)acetanilide. The light sensitive element is kept at 120°F and 50% relative humidity for various periods of time and then exposed
30 and processed at 35°C in a three-step process of colored development (45 seconds), bleach-fix (45 seconds), and stabilization (90 seconds) followed by drying (60 seconds) at 60°C.

- The formulations for the above processing
35 solutions are as follows:

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(1) Color developers:

Lithium salt of sulfonated polystyrene (30% by wt)	0.25mL
Triethanolamine	11.0 mL
N,N diethylhydroxylamine (85% by wt)	6.0 mL
Potassium sulfite (45% by wt)	0.5 mL
Color developing agent 4 (N-ethyl N-2 methanesulfonylaminoethyl) 2 methyl phenylenediaminesesquisulfate monohydrate	5.0 g
Kodak Ektaprint 2 Stain-Reducing Agent (a stilbene material commercially available from Eastman Kodak Co.)	2.3 g
Lithium sulfate	2.7 g
Potassium chloride	2.5 g
Potassium bromide	0.025 g
Kodak Anti Cal No. 5 (an organic phosphonic acid material commercially available from Eastman Kodak Co.)	0.8 mL
Potassium carbonate	25.0 g
Water to total of 1 liter, pH adjusted to	10.12

(2) Bleach-fix:

Ammonium thiosulfate	58.0 g
Sodium sulfite	8.7 g
Ethylenediaminetetraacetic acid ferric ammonium salt	40.0 g
Acetic acid	9.0 mL
Water to total 1 liter, pH adjusted to	6.2

(3) Stabilizer:

Sodium citrate	1.0 g
Dearside (a biocide produced by Rohm and Haas)	45.0 ppm
Water to total 1 liter, pH adjusted to	7.2

The developed element exhibits excellent
5 resistance crazing.

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What is Claimed is:

1. A resin coated substrate for photographic prints comprising a paper-like substrate coated with a layer of polyolefin resin, said layer including at least about 0.01 percent by weight of a hindered amine light stabilizer from about 5 to about 25 percent by weight of a titanium dioxide and from about 0.5 to about 4 percent by weight of zinc oxide.
2. The resin coated substrate of claim 1 the hindered amine light stabilizer is present in the amount of from 0.01 to about 2 percent by weight.
3. The resin coated substrate of claim 1 wherein the zinc oxide is present in the amount of from about 0.5 to about 3.5 percent by weight.
4. The resin coated substrate of claim 1 wherein the titanium dioxide is present in the amount of from about 8 to about 18 percent by weight.
5. The resin coated substrate of claim 1 wherein the titanium dioxide is present in the amount of from about 9 to about 15 percent by weight.
6. The resin coated substrate of claim 1 wherein the hindered amine light stabilizer contains a 2,2,6,6-tetramethyl-piperidine moiety.
7. The resin coated paper of claim 1 wherein the polyolefin is polyethylene.
8. The resin coated substrate of claim 1 wherein the hindered amine light stabilizer is bis(2,2,6,6-tetramethyl-4-piperidinyl)sebacate, bis(1,2,2,6,6,-pentamethyl-4-piperidinyl)sebacate, n-butyl-(3,5-di-tert-butyl-4-hydroxybenzyl)bis-(1,2,2,6,6-pentamethyl-4-piperidinyl)malonate, dimethyl succinate polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol, N-N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-1,6-hexanediamine polymer with 2,4,6-trichloro-1,3,5-triazine and 2,4,4-trimethyl-1,2-pentanamine or poly(6-morpholino-s-triazine-2,4-diyl)[(2,2,6,6-tetra-methyl-4-piperidyl)imino]hexamethylene[(2,2,6,6-tetra-methyl-4-piperidyl)imino]].

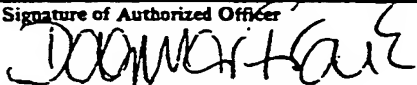
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9. A silver halide light sensitive element comprising a paper-like substrate coated with a layer of polyolefin resin, said layer including from at least 0.01 percent by weight of a hindered amine light stabilizer from about 5 to about 25 percent by weight of a titanium dioxide and from about 0.5 to about 4 percent by weight of zinc oxide and at least one light sensitive silver halide emulsion layer on the polyolefin resin layer.
10. The light sensitive element of claim 9 wherein the hindered amine light stabilizer is present in the amount of from about 0.01 to about 2 percent by weight.
11. The light sensitive element of claim 9 wherein the zinc oxide is present in the amount of from about 0.5 to about 3.5 percent by weight.
12. The light sensitive element of claim 9 wherein the titanium dioxide is present in the amount of from about 8 to about 18 percent by weight.
13. The light sensitive element of claim 9 wherein the titanium dioxide is present in the amount of from about 9 to about 15 percent by weight.
14. The light sensitive element of claim 9 wherein the hindered amine light stabilizer contains a 2,2,6,6,-tetramethylpiperidine moiety.
15. The light sensitive element of claim 9 wherein the hindered amine light stabilizer is bis(2,2,6,6-tetramethyl-4-piperidinyl)sebacate, bis(1,2,2,6,6,-pentamethyl-4-piperidinyl)sebacate, n-butyl-(3,5-di-tert-butyl-4-hydroxybenzyl)bis-(1,2,2,6,6-pentamethyl-4-piperidinyl)malonate, dimethyl succinate polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol, N-N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-1,6-hexanediamine polymer, with 2,4,6-trichloro-1,3,5-triazine and 2,4,4-trimethyl-1,2-pentanamine or poly(6-morpholino-s-triazine-2,4-diyl)[(2,2,6,6-tetra-methyl-4-piperidyl)imino]hexamethylene[(2,2,6,6-tetra-methyl-4-piperidyl)imino]].

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/06928

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 G03C1/79; D21H19/38; C08K3/22		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	G03C ; D21H ; C08K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	EP,A,0 085 523 (THE WIGGINS TEAPE GROUP LIMITED) 10 August 1983 cited in the application see the whole document ---	1-15
Y	EP,A,0 290 388 (CIBA-GEIGY AG) 9 November 1988 see page 1, line 22 - line 39 ---	1-15
Y	GB,A,2 048 278 (THE WIGGINS TEAPE GROUP LIMITED) 10 December 1980 cited in the application see page 2, line 42 - line 51 ---	8,15
	-/--	
<p>¹⁰ Special categories of cited documents : ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 28 OCTOBER 1992		Date of Mailing of this International Search Report 01. 12. 92
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer 

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	CHEMICAL ABSTRACTS, vol. 100, no. 6, February 1984, Columbus, Ohio, US; abstract no. 43001b, page 541 ;column 1 ; see abstract & SU,A,1 031 986 30 July 1983	1
A	US,A,3 376 250 (GORDON C NEWLAND ET AL) 2 April 1968 see the whole document	1

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9206928
SA 64003

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The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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